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DEC 82 TR-11 N00014-78-C-0325

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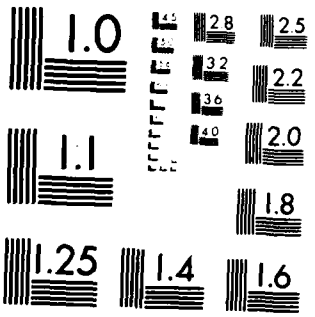

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1 REPORT NUMBER: 11	2 GOVT ACCESSION NO.: AD-A122755	3 RECIPIENT'S CATALOG NUMBER:
4 TITLE (and Subtitle): SPECTRA FROM MOLECULAR DYNAMICS (12)		5 TYPE OF REPORT & PERIOD COVERED: Technical
		6 PERFORMING ORG. REPORT NUMBER:
7 AUTHOR(s): Peter H. Berens, John P. Bergsma and Kent R. Wilson		8 CONTRACT OR GRANT NUMBER(s): ONR-N00014-78 C-0325
9 PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of California, San Diego, La Jolla, CA 92093		10 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11 CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Arlington, VA 22217		12 REPORT DATE: December 1982
		13 NUMBER OF PAGES: 4
14 MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15 SECURITY CLASS. (of this report): Unclassified
		15a DECLASSIFICATION DOWNGRADING SCHEDULE:

16 DISTRIBUTION STATEMENT (of this Report)

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17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18 SUPPLEMENTARY NOTES

To be published in Time-Resolved Vibrational Spectroscopy, ed. G. Atkinson (Academic Press, New York, 1982), in press.

19 KEY WORDS (Continue on reverse side if necessary and identify by block number)

molecular dynamics
infrared spectra
electronic spectra
Raman spectra
vibrational spectroscopy
photodissociation

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Contract N00014-78 C-0325

TECHNICAL REPORT NO. 11

SPECTRA FROM MOLECULAR DYNAMICS

BY

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SPECTRA FROM MOLECULAR DYNAMICS[1]

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Following the work of Roy Gordon(1) we are accustomed to deducing molecular dynamics from spectra. Here we take the inverse approach and compute spectra from molecular dynamics. Specifically, from atomic trajectories we compute infrared, electronic, and nonresonance Raman spectra. Fig. 1 illustrates the general technique. From an initial set of atomic positions and velocities and the forces among the atoms we calculate from Newton's second law the atomic trajectories. For infrared or electronic absorption spectra we connect to the radiation field through the dipole moment μ, and for Raman spectra we connect through the polarizability tensor **P**. The technique can be viewed as an expression of classical linear response theory or as an exercise in classical electromagnetic theory. We use a power spectral approach symbolized as D[ ], taking advantage of fast Fourier analysis with windowing and associated corrections(2, 3). An average, symbolized by $< >$, of the spectrum is taken over the ensemble appropriate to the experimental conditions (for example a constant temperature and density) and simple quantum corrections to the spectra are applied where needed.

Molecular absorption spectra can be rotational, vibrational, and electronic. All normally involve interaction of nuclear position and radiation field through the dipole moment. Fig. 2 shows an example of a gas phase vibrational-rotational infrared spectrum. Elsewhere(2) we have also computed pure rotational absorption spectra and have extended vibrational and rotational infrared spectral calculations to the liquid phase.

[1] *We thank the National Science Foundation, Chemistry, the Office of Naval Research, Chemistry, the National Aeronautics and Space Administration, Ames Research Center, and the National Institutes of Health, Division of Research Resources for providing the support which has made this work possible.*

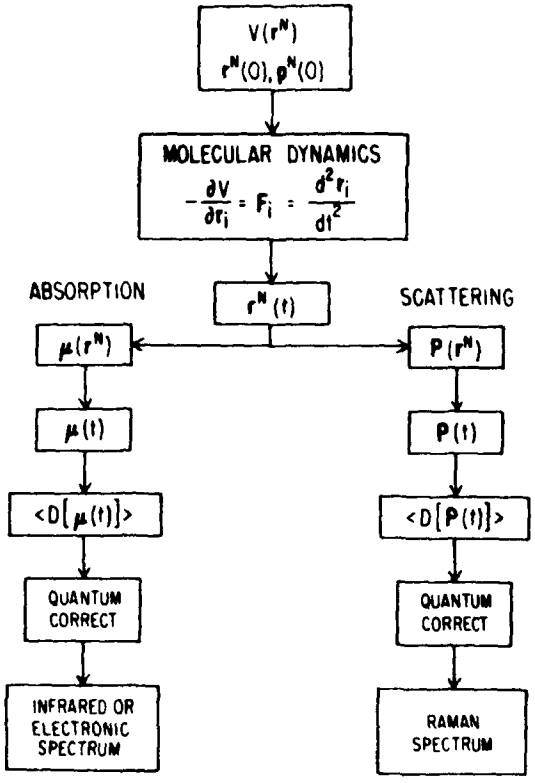

FIGURE 1. Calculation of absorption and scattering spectra from molecular dynamics.

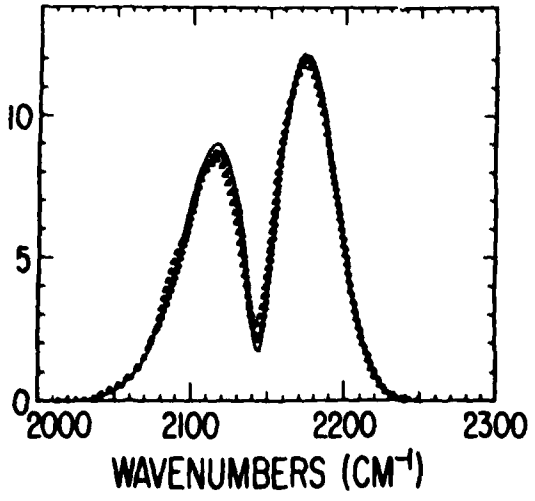

FIGURE 2. Band contours for the infrared gas phase CO fundamental vibrational-rotational band(2). The triangles show our essentially classical molecular dynamics calculation, the solid line shows an accurate quantum calculation and the dots show the experimental measurement(4).

Fig. 3 shows the computed equilibrium and picosecond transient electronic absorption spectra of I_2 photodissociation in liquid Xenon. The connection to the radiation field is through the transition dipole moment, and the Iodine atoms are sufficiently massive that quantum corrections are negligible. In addition to one photon, or absorption spectra, we can also compute two photon, or scattering, processes, as illustrated in Fig. 3 for a liquid solution Raman spectrum.

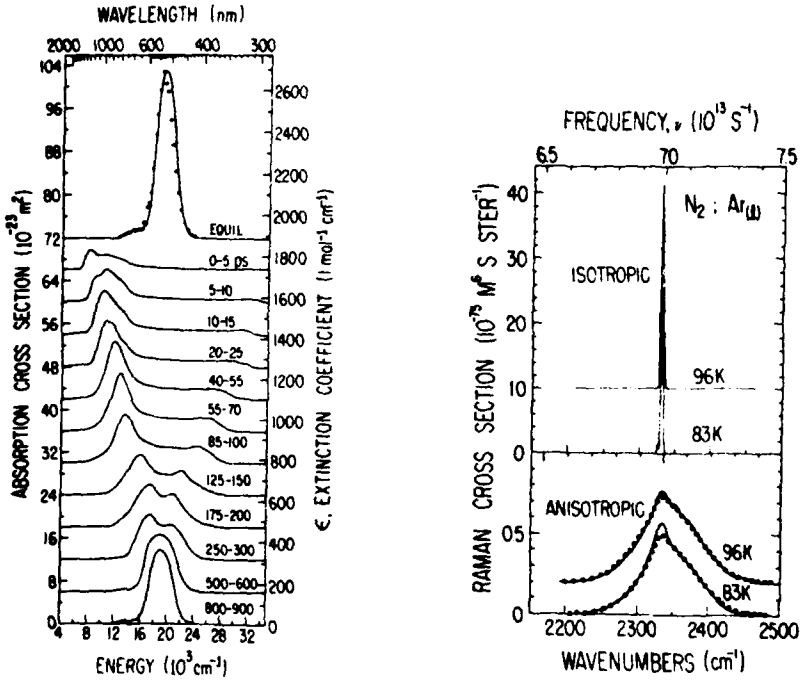

FIGURE 3. The left panel shows the electronic absorption spectrum for I_2 in liquid Xenon, made up of transitions from the ground state to the excited A, B, and B'' states(5). The computed equilibrium room temperature spectrum is shown at top, with the gas phase I_2 band contour as measured by Tellinghuisen(6) shown as dots. Below are the computed transient spectra from 0 to 900 picoseconds for the reaction sequence beginning with photodissociative excitation to the A state, then either I atom escape or solvent caging followed by recombination to form a highly vibrationally excited I_2 molecule which loses its energy to the solvent. The right panel shows the isotropic and anisotropic Raman spectra of N_2 in liquid Ar. The lines show the spectra computed from molecular dynamics(3) and the dots show the measurements of Hanson and McTague(7).

We have shown, for systems for which the potential energy and the appropriate connection to the radiation field (dipole moment or polarizability) are known sufficiently accurately, that infrared, electronic, and nonresonance Raman spectra can be computed from classical molecular dynamics followed by simple quantum corrections to the spectra. Note that no adjustable parameters are needed for any of the spectra presented here. These essentially classical spectra can be compared to experimentally measured spectra to check that the underlying computed dynamics are correct, and the agreement illustrated here indicates that a basically classical view of the atomic motions involved in these spectra is a useful one, in harmony with our well calibrated physical intuition.

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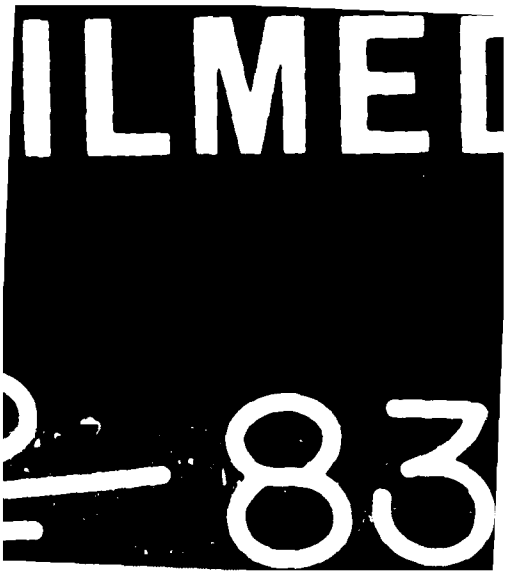
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